High Temperature Polymeric Materials for Space Transportation Propulsion Applications

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ABSTRACT

High temperature polymer matrix composites are attractive materials for space transportation propulsion systems because of their low density and high specific strength. However, the relatively poor stability and processability of these materials can render them unsuitable for many of these applications. New polymeric materials have been developed under the Propulsion Research and Technology Program through the use of novel resin chemistry and nanotechnology. These new materials can significantly enhance the durability and weight and improve the processability and affordability of propulsion components for advanced space transportation systems.

INTRODUCTION

High temperature polymers and fiber reinforced polymer matrix composites are potentially attractive alternatives to more traditional aerospace materials for use in weight critical propulsion and airframe components for future space transportation systems. Because of their low densities (25% that of titanium) and high specific strengths, use of these composites in place of more traditional aerospace materials can lead to as much as a 20- 30% reduction in component weight. While high temperature polymer matrix composites are fairly new to most space transportation systems, they have been successfully utilized in both military (engine and airframe) and commercial (engine) aircraft components. For example, graphite reinforced PMR-15 composites have been used in the outer bypass ducts for General Electric's F-404 engine for Navy's F-18 fighter, the core cowl for Snecma's CF6-80-A3 commercial aircraft engine, and on engine access doors for the B-52 bomber.

Despite their attractive attributes, high temperature polymer matrix composites have a few limitations that impact their usefulness in space transportation airframe and propulsion components. The poor thermal-oxidative stability of conventional high temperature polymer matrix composites limits their use to components seeing operating temperatures no higher than 450-500°F, well below the temperatures experienced by space transportation propulsion and

airframe components. This requires that these components be insulated to protect them from high temperatures experienced in both service environments. Insulation adds parasitic weight which can negate much of the weight savings realized by the use of lightweight materials. In addition, conventional high temperature polymer matrix composites require processing methods which are labor intensive and costly and are not amenable to the fabrication of large structures typical of space transportation systems.

High temperature polymer matrix composite research supported under the Propulsion Research and Technology Project of NASA's Advanced Space Transportation Program has focused on improving the high temperature stability and manufacturability of these materials in order to make them more suitable for use in space transportation propulsion systems. This research has employed a combination of novel polymer chemistry and low cost manufacturing methods to improve the processability of high temperature polymer matrix composites and on the use of nanotechnology and innovative fiber architectures to enhance their high temperature durability. This paper summarizes the accomplishments of this research activity.

RESULTS AND DISCUSSION

High Temperature Polymers with Improved Processability

Processing methods typically employed in the fabrication of high temperature polymer matrix composites involve autoclave or compression molding of prepreg based materials. These methods require a considerable amount of hand labor and, as a result, are costly. Cost effective methods, such as resin transfer molding, vacuum assisted resin transfer molding and resin film infusion, have been developed that can reduce manufacturing costs by as much as 50% over traditional prepreg based methods. These low cost fabrication techniques are also more amenable to the fabrication of large structures. Resin transfer molding (RTM) involves infiltrating a woven or braided perform in a closed mold with liquid resin, followed by curing (cross-linking) of the resin at high temperatures. Resins that are to be processed using RTM should have melt viscosities no higher than 30 Poise. In addition, these melt viscosities should be stable for long enough times (typically an hour or more) to allow complete infiltration and wetting of the preform.

Typical high temperature polymers, such as PMR-15 or PETI-5, have melt viscosities in excess of 1000 Poise, nearly 100 times higher than the limit for RTM processing! New resins are needed with melt viscosities amenable to RTM (or other resin infusion based processes) and good high temperature stability and performance.   Such a combination of properties is not easy to obtain since those molecular structures that could be utilized to achieve low melt viscosity can have an adverse effect on high temperature stability and glass transition temperature.
A number of approaches have been employed to reduce the melt viscosity of high temperature polymers.   These include the incorporation of molecular twists, kinks, asymmetric groups and branching[1]. Two of these approaches, molecular twists and branching, have been explored in parallel and as a combined approach, i.e., twists and branching were incorporated within the same molecular structure. The structures of twisted, BPDA, and branched, TAB, and examples of other monomers used in this study are shown in Figure 1.
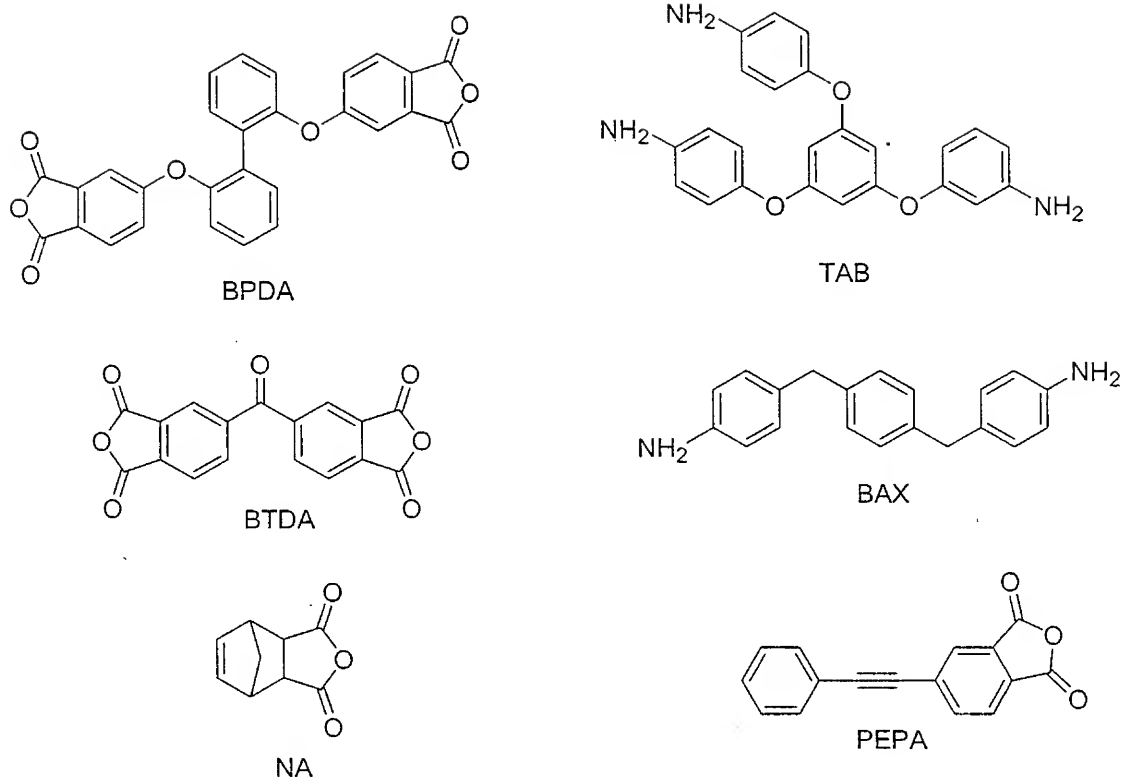
Figure 1. Chemical structures of monomers used in the synthesis of RTM processable high temperature polymers.

Oligomers were prepared from these monomers and a reactive endcap, either NA or PEPA. An example of a viscosity profile for one of these resins is shown in Figure 2. This profile was generated using parallel plate rheometry on a 0.5 gram sample of resin. The sample is heated under conditions that simulate the cure cycle for the resin and the rheological properties are measured as the sample is taken through this cure cycle. Typically these oligomers undergo a melt at temperatures around 250°C and reach a minimum melt viscosity at about 270°C. In order to be able to process complex parts, it is desirable that this melt viscosity remain stable for at least 1 hour at the melt processing temperature.
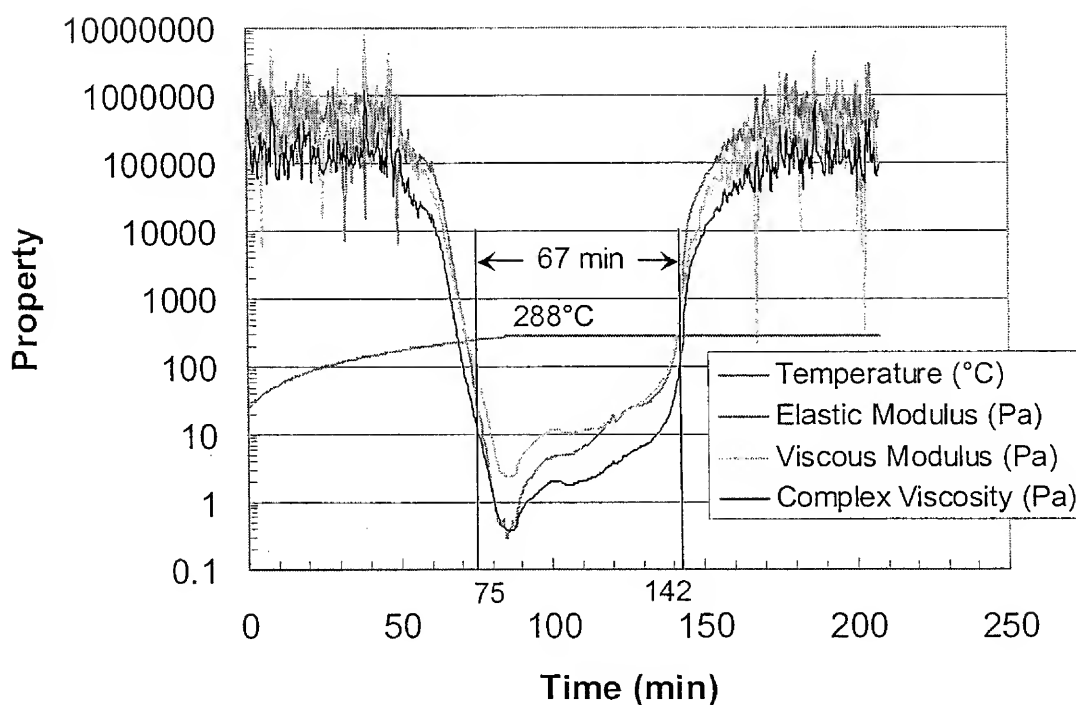
Figure 2. Typical viscosity temperature profile for low melt viscosity polyimide resins generated by parallel plate rheometry.

Resin formulations were evaluated based upon their melt viscosity and glass transition temperature and one resin system was down-selected for evaluation in resin transfer molding studies. A Design of Experiments approach was used to determine the optimum formulation in each of the three approaches, i.e., twisted, branched and combined[2]. The properties of the best formulation from each approach are presented in Table 1. Introduction of "twisted" BDPA biaryl units into the polymer backbone significantly reduced the melt viscosity of the resin. Unfortunately, the glass transition temperatures of these resins were also low, no higher than 260°C, which limits their usefulness in high temperature propulsion applications. On the other hand, resins containing branching, through the introduction of TAB units, possessed Tg's close to 320°C. However, the melt viscosity of these resins was significantly higher than the desired maximum level of 30 Poise. A combination of both molecular twists and branching afforded a resin with low enough melt viscosity for RTM processing and a reasonably high glass transition temperature.

Resin	Melt Viscosity, Poise	Tg, °C
PBDA-15 (Twisted)	34	260
TAB-Lo (Branched)	>100	319
TAB-PBDA (Combined)	16	320

Table 1. Comparison of melt viscosity and Tg of optimized formulations containing twisted, branched units and a combination of the two.

Carbon fabric (T650-35, 8HS) reinforced laminates were prepared from this resin system and their mechanical properties were evaluated at room and elevated temperatures. A comparison of the short beam shear strength of T650-35 reinforced carbon fabric composites

prepared with the optimized resin system (BAX-TAB-10), a leading RTM processable high temperature resin (PETI-330) and a baseline RTM processable bismaleimide (5270-1) is shown in Figure 3. At all of the test temperatures, both the PETI-330 and BAX-TAB composites had superior properties to the baseline bismaleimide composite. The properties of both the BAX-TAB and PETI-330 composites were comparable at room temperature and 232°C, however at 288°C the properties of PETI-330 composite were slightly higher than the BAX-TAB composite due to the higher Tg value for PETI-330 (330 vs. 320°C). Efforts are underway to increase the glass transition temperature of these materials by modification of both the matrix resin chemistry and the cure and post-cure conditions.
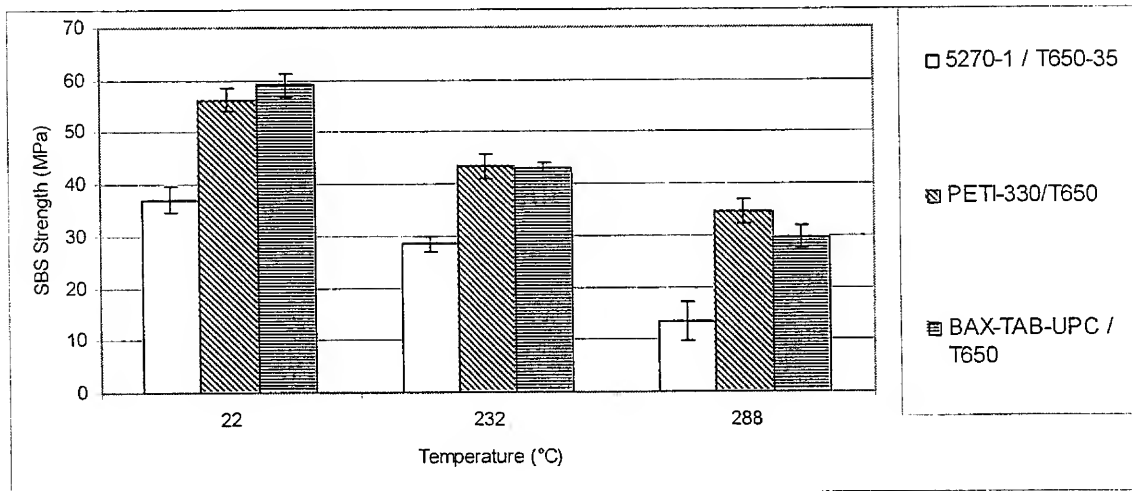

Figure 3. A comparison of the short-beam shear properties of T650-35/8HS carbon fabric composites made with 5270-1 BMI, PETI-330, and BAX-TAB.

In an attempt to develop polyimides and composites with higher glass transition temperatures, a series of phenylethynyl endcapped polyimides containing a fluorinated monomer were evaluated. This study led to the identification of a promising new composite material, HFPE-II-52, with good retention of mechanical properties at temperatures as high as 343°C[3]. A comparison of the unnotched compression and shear strength of T650-35 carbon fabric reinforced HFPE and 5270-1 laminates is shown in Figure 4.
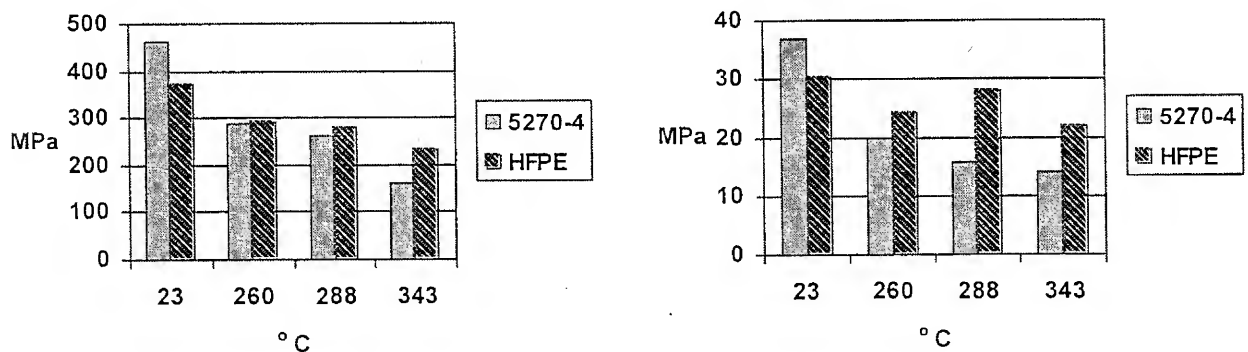

Figure 4. A comparison of the unnotched compression (left) and interlaminar shear strength (right) of T650-35 carbon fabric reinforced HFPE and 5270 laminates at room and elevated temperatures.

HFPE composites were readily processed using a modified resin film infusion, RFI, process. Like resin transfer molding, RFI requires resins with low and stable melt viscosities. The melt viscosity for neat HFPE resin is too high for either process. However, adding a small amount of solvent (less than 10%) to the resin plasticizes it and reduces the viscosity enough to enable the use of An RFI process which had been modified to allow for removal of the solvent. A variety of different representative carbon fabric reinforced components have been prepared with HFPE resin using this modified process (Figure 5).
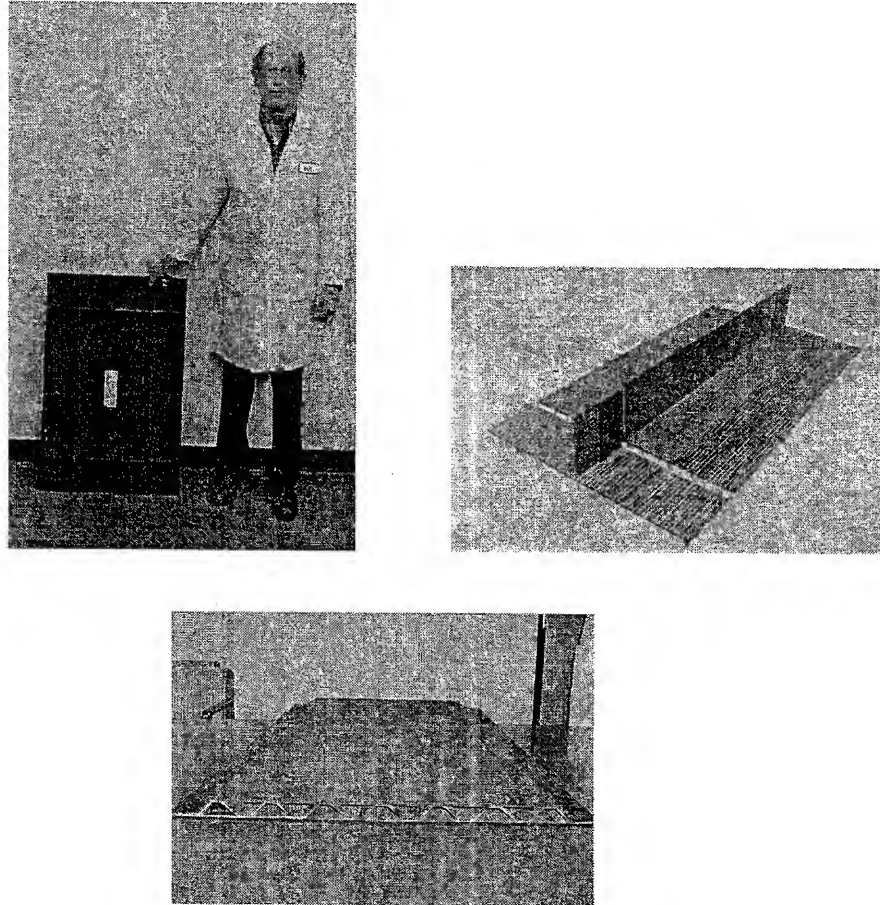

Figure 5. HFPE composite components prepared via Resin Film Infusion

High Temperature Polymers and Composites with Improved Durability High Temperature Performance

Oxidation of the polymer at elevated temperature is the dominant degradation mechanism in polymer matrix composites and limits their use temperature. Over the years, a variety of approaches have been employed to exclude oxygen from these composites and prevent their degradation. Most of these have involved the application of a ceramic or metal coating onto the composite. However, the severe mismatch in coefficient of thermal expansion between the metal or ceramic coating and the composite substrate compromises coating durability and causes it to eventually spall off of the composite substrate.

Recent research has demonstrated that addition of small amounts (less than 10 weight percent) of organically modified clays to a polymer, such as Katpon, significantly reduces the permeability of oxygen through the polymer[4]. These polymer/clay nanocomposites could provide

the needed oxidation barrier for the composite substrate and could be applied either as a coating or used as the matrix resin in a fiber or fabric reinforced composite. Coatings made from these nanocomposites should not suffer from the durability issues experienced in previous coatings studies since the coefficient of thermal expansion of the nanocomposite should be fairly close to that of the base polymer.

Organically modified clays were added to a PMR-15 polyimide matrix resin and T650-35-carbon fiber reinforced composites were made from the nanocomposite matrix resin. The effects of this clay addition on the thermal oxidative stability of both the neat resin and composite are shown in Figure 6. Addition of clay to both the neat resin and the composite significantly reduced oxidative weight loss. Neat resin weight loss was reduced by 14.5% with the addition of 5 weight percent clay, while the composite's weight loss was reduced by 25% with only 1 weight percent clay[5].
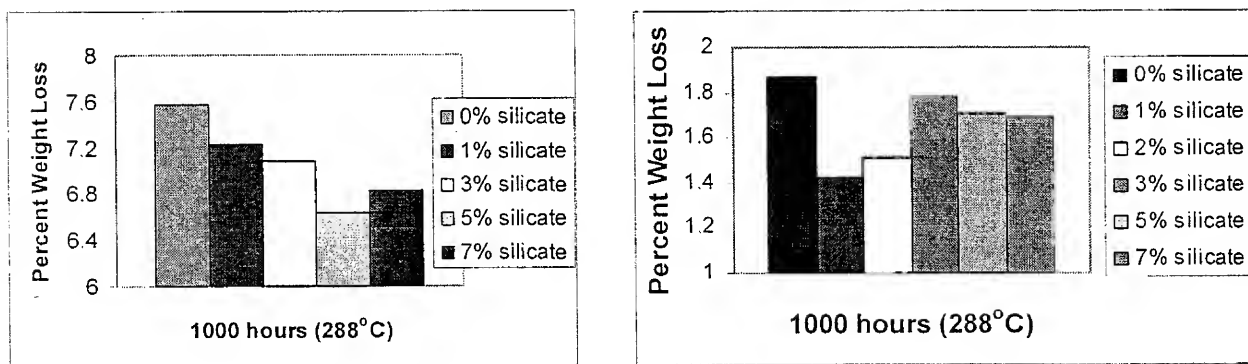

Figure 6. Effects of added organically modified clay on the weight loss of PMR-15 neat resin (left) and T650-35 reinforced composites (right) after 1000 hours at 550°F (288°C).

Some insight into the origin of this weight loss reduction can be seen in the SEM photomicrographs shown in Figure 7. Both samples are of composites aged for 500 hours in air at 550°F (288°C). In the absence of clay, the composite samples show a degradation pattern typical of high temperature polyimide composites – formation of an oxidation layer (white surface layer) and microcracking produced by internal stresses between the oxidation layer and bulk composite. This microcracking exposes more of the composite to oxidation and leads to increased weight loss. However, formation of the oxidation layer in the composite is suppressed with the addition of clay. In addition, the composite sample containing clay exhibited no signs of microcracking. As a result, oxidative weight loss is reduced in the samples which contained clay.
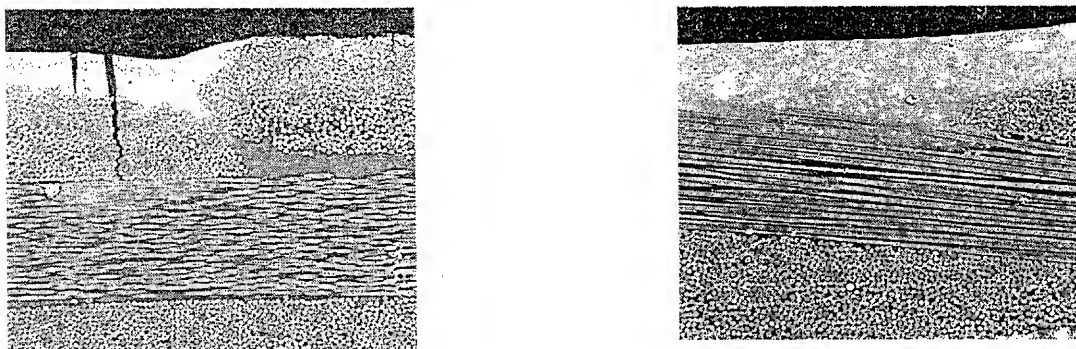

Figure 7. SEM photomicrographs of carbon fiber reinforced polyimide composites after 500 hours aging in air at 550°F (288°C), without clay (left) and with clay (right).

Addition of clay also improved the mechanical properties of the composites both at room and elevated temperatures. The effect of added clay on the flexural strength and modulus of T650-35 carbon fiber reinforced PMR-15 composites is shown in Figure 8. Addition of 1 weight percent clay increases both the room temperature and 550°F (288°C) flexural strength of the PMR-15 composites by 30%. A similar increase in flexural modulus was also observed at the same clay loading level.
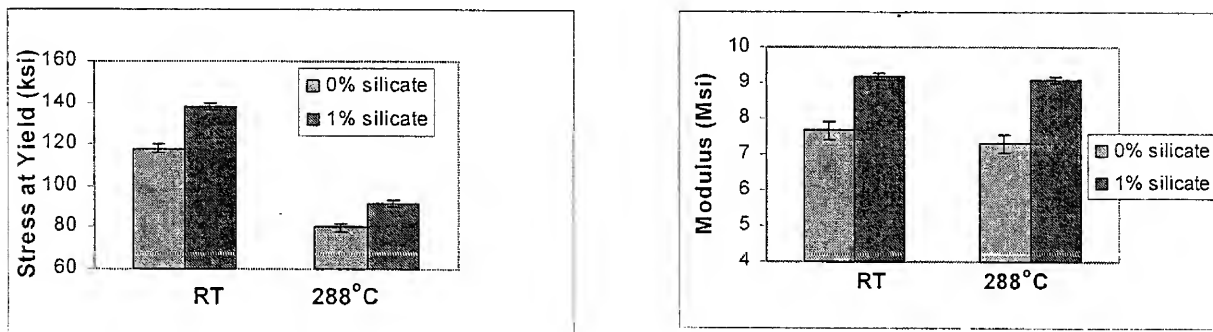

Figure 8. Effect of added clay on the flexural strength (left) and modulus (right) of T650-35 carbon fiber reinforced PMR-15 composites.

SUMMARY AND CONCLUSIONS

Significant improvements in the processability and durability of high temperature polymer matrix composites can be achieved through the use of novel resin chemistry and nanotechnology. Utilizing a combination of molecular twists and branching provided resins with both low melt viscosities and good high temperature properties. These resins can be processed using cost-effective techniques such as resin transfer molding into propulsion components suitable for use at temperatures as high as 550°F. Ultrahigh temperature resins have been developed by incorporating fluorinated monomers and stable end-caps into the polymer. Carbon fabric reinforced composites made with this resin show outstanding retention of mechanical properties at temperatures as high as 650°F. Addition of small amounts of organically modified clays to high temperature polyimides and carbon fiber reinforced composites led to significant enhancements in their high temperature stability. In addition, composites made with the clay modified polyimide had 30% higher flexural strength and modulus (at both room temperature and 550°F) than composites without added clay. Use of these advanced materials will enable the cost effective construction of space transportation propulsion components with enhanced durability and performance.

FUTURE WORK

Recent Value Stream Planning for the Next Generation Launch Technologies Propulsion Research and Technology Program identified a high priority need for the development of polymer matrix composites and adhesives that are stable for 100 hours at 700-750°F. Use of these materials in backing structures for propulsion system flow path components can enable significant component weight reductions. These requirements can be met by building upon the successes of the previous high temperature polymeric materials development activities described in this paper. For example, addition of organically modified clays to the ultrahigh temperature (HFPE) composites should enhance their stability and high temperature mechanical properties enough to make them suitable for use at higher temperatures. Low melt viscosity resins can be modified to increase their high temperature stability in order to develop high temperature adhesives. Design databases must be developed for the most promising composites and adhesives. In addition, these materials must be validated through component fabrication and engine testing.

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